



Short communication

MWCNT-supported phthalocyanine cobalt as air-breathing cathodic catalyst in glucose/O₂ fuel cellsKamal Elouarzaki^a, Raoudha Haddad^b, Michael Holzinger^a, Alan Le Goff^a, Jessica Thery^b, Serge Cosnier^{a,*}^a Département de Chimie Moléculaire UMR-5250, ICMG FR-2607, CNRS-Université Joseph Fourier, BP-53, 38041 Grenoble, France^b LCI/DTNM/LITEN/CEA, 17 Av. des Martyrs, 38054 Grenoble, France

H I G H L I G H T S

- New generation of non-enzymatic glucose fuel cell using anionic exchange membrane.
- Simple and highly efficient glucose fuel cells using abiotic catalysts are obtained.
- Anion exchange membrane shows superior power density compared to cationic one.
- We report the highest stability described for an alkaline glucose fuel cell.

A R T I C L E I N F O

Article history:

Received 12 September 2013

Received in revised form

16 December 2013

Accepted 26 December 2013

Available online 4 January 2014

Keywords:

Glucose fuel cell

Carbon nanotube

Cobalt phthalocyanine

Oxygen reduction

Electrocatalysis

A B S T R A C T

Simple and highly efficient glucose fuel cells using abiotic catalysts and different ion exchange membranes were designed. The glucose fuel cells are based on a multi-walled carbon nanotube (MWCNT)-supported cobalt phthalocyanine (CoPc) cathode and a carbon black/platinum (C/Pt) anode. The electrocatalytic activity of the MWCNT/CoPc electrode for oxygen reduction was investigated by cyclic and linear sweep voltammetry. The electrochemical experiments show that CoPc exhibits promising catalytic properties for oxygen reduction due to its high overpotential and efficiency at reduced metal load. The MWCNT/CoPc electrodes were applied to the oxygen reduction reaction as air-breathing cathode in a single-chambered glucose fuel cell. This cathode was associated with a C/Pt anode in fuel cell configurations using either an anion (Nafion®) or a cation (Tokuyama) exchange membrane. The best fuel cell configuration delivered a maximum power density of 2.3 mW cm⁻² and a cell voltage of 0.8 V in 0.5 M KOH solution containing 0.5 M glucose using the Tokuyama membrane at ambient conditions. Beside the highest power density per cathodic catalyst mass (383 W g⁻¹), these glucose fuel cells exhibit a high operational stability, delivering 0.3 mW cm⁻² after 50 days.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The importance of electrochemical oxidation of sugars has been emphasized in the fields of analytical chemistry and fuel cell technology [1]. Glucose is one major biomass component that potentially possesses a large density of chemical energy. Moreover, it is nontoxic, non-flammable, inexpensive, and easy to handle. Among clean alternative sources of sustainable and renewable energy, the conversion of chemical energy into electrical energy by glucose fuel cells is seriously considered. Electricity is thus generated efficiently from the oxidation of glucose coupled to the

reduction of oxygen to water. Moreover, taking into account that glucose and oxygen are both present in physiological fluids, glucose fuel cells can power implanted medical devices.

Among challenges dealing with the improvements in power outputs of glucose fuel cells is the choice of the electrocatalyst for glucose oxidation and oxygen reduction as well as the most suitable ion conducting membrane. While Pt and gold metals or alloys has been well documented at the bioanode for electrocatalytic oxidation [2–4], the cathode is mainly composed of carbon or platinum-based material which are the best electrocatalyst for oxygen reduction reaction (ORR) both in acid and alkaline fuel cells because of their high electrocatalytic activity and chemical stability. This represents an important issue because a protective membrane is needed to avoid non-specific catalytic side reactions at both electrodes that drastically decrease the power output of such devices.

* Corresponding author.

E-mail address: serge.cosnier@ujf-grenoble.fr (S. Cosnier).

In general, one major drawback of metal catalysts in glucose fuel cells is the non-specificity of the material towards both, oxygen and glucose. Moreover, the oxygen reduction often constitutes a limitation for the power of glucose fuel cells due to the low oxygen concentration in water.

To avoid these selectivity issues, only few examples have shown that molecular catalyst such as metal-porphyrin complexes are more specific towards oxygen reduction in complex medium compared to catalytic metal cluster electrodes [5]. We recently proposed the use of porphyrin-based molecular catalyst at both electrodes of a glucose fuel cell [6], where the catalyst for the bioanode was focused. Here, we studied the use of a phthalocyanine cobalt complex immobilized on multi-walled carbon nanotube (MWCNT) as cathodic catalyst for oxygen reduction in a glucose fuel cell. The alkaline glucose/O₂ fuel cell presented in this work contains as anode commercial available Pt modified carbon black for the oxidation of glucose. Up to now, the mostly used membranes at industrial scale are based on perfluorosulfonic ionomers [7–9]. Such cationic membranes called Nafion® have many advantages such as good current profiles, mechanical endurance, and chemical durability. However, for fuel cell applications these membranes are susceptible to loose water which causes a decrease in conductivity and the penetration of electrolyte through the membrane reducing the open circuit voltage of the fuel cell. Another recent generation of anion exchange membranes presents an interesting way to solve some drawbacks of Nafion [9,10]. We have thus investigated the effect of two types of ion exchange membranes: an anionic (Tokuyama) and a cationic (Nafion®) exchange membranes on the performance of our specific glucose fuel cell. Finally an air-breathing setup was designed to optimize the supply of glucose and oxygen. Thus, glucose was oxidized in a flow-through glucose solution chamber while oxygen from air is reduced at an air-breathing cathode by cobalt phthalocyanine (CoPc).

2. Materials and methods

2.1. Chemicals

Commercial grade thin Multi-Walled Carbon Nanotubes (MWCNTs) (average 9.5 nm diameter, purity >95%), obtained from Nanocyl were used as received without any purification step. The platinum modified carbon black (60% Pt) was furnished by Johnson Matthey Fuel cells. Nafion® N-115 membranes based on perfluorosulfonic acid/PTFE copolymer in acid form were provided by DuPont™. These membranes are 127 µm thick and have a standard exchange capacity of 0.9 meq/g and a conductivity of 74 mS/cm [11]. The anionic membranes were provided by Tokuyama-Neosepta (Astom Corp) and are 27 µm thick. The exchange capacity of the membrane is 1.7 meq/g with a conductivity of 7 mS/cm and its water swelling is of 40%. Cobalt(II) phthalocyanine, Nafion®, 1-methyl-2-pyrrolidinone (NMP), D-glucose, and potassium hydroxide (KOH) were of analytical grade and purchased from Sigma–Aldrich. Ultrapure water was obtained from a Milli-Q Purelab UHQ (Elga) with a resistivity of 18.2 MΩ cm⁻¹.

2.2. Electrochemical measurements

Cyclic voltammetry (CV) was performed in a conventional three-electrode cell equipped with a glassy carbon (GC) electrode (geometric area = 0.071 cm²), a platinum wire as counter-electrode and a saturated calomel electrode (SCE) as reference electrode. The surface of the GC electrodes was polished using a 2 µm diamond paste, purchased from Presi (France), washed with water using an ultrasonic bath, and rinsed sequentially with acetone and ethanol.

The measurements were performed in aqueous KOH solutions. The pH was continuously monitored during all experiments by a pH-meter (GLP, CRISON). The solutions were purged respectively using high-purity argon or oxygen prior to each experiment and an argon or oxygen flow was maintained over the solution during the whole experiment.

The CVs measurements were performed at 25 °C with an Autolab electrochemical analyzer (Eco Chemie, Utrecht, The Netherlands) controlled by GPES software (Eco Chemie).

Electrochemical impedance spectroscopy (EIS) is used to analyze the internal resistances throughout the fuel cell using the different ion exchange membranes. The EIS spectra were performed using two electrodes because the designed cell was not accommodated for the inclusion of a reference electrode. The anode was used as a pseudo-reference electrode. The frequency range of the impedance spectra spanned from 1000 kHz to 100 mHz with an AC amplitude of 20 mV. The frequencies were spaced in logarithmic progression with 10 points per frequency decade. The EIS measurements were performed using a Biologic VMP 3B-5 potentiostat controlled by EC-lab software.

2.3. Preparation of the fuel cell

The MWCNT/CoPc suspension was prepared using the following method: MWCNTs (5 mg) were added to 1 ml of N-Methyl-2-Pyrrolidone (NMP) solvent containing CoPc complex (1 mg) and 5 µL Nafion® solution (the Nafion solution contains 5% Nafion, 25% 2-propanol, 25% n-propanol, 45% water). The suspension was homogenized by sonication for 30 min. After sedimentation of the precipitates, the resulting supernatant was used as catalyst ink. For the electrochemical investigations, 10 µL of this suspension was deposited onto a freshly polished GC disk electrode (3 mm diameter) by drop-casting and the solvent was removed under reduced pressure.

For the glucose fuel cell experiments, the catalytic MWCNT/CoPc ink was deposited onto the side of a polyelectrolyte membrane to elaborate the biocathode. Two membranes were examined: a Nafion® membrane and a Tokuyama membrane. At the anodic compartment of the fuel cell, an ink based on carbon (Vulcan XC-72) covered with platinum nanoparticles (60% Pt) was used. The carbon black/Pt nanoparticles ink (C/Pt) was spread providing 600 µg cm⁻² Pt coverage. One layer of the deposited (C/Pt) consists of 13 µL of ink per square centimetre. A porous gold electron collector (250 nm thickness) was then deposited via magnetron sputtering on both, the anode and cathode sides for an optimal electron collection. The anodic compartment was filled with an alkaline glucose solution (0.5 M glucose/0.5 M KOH) under constant flow using a peristaltic pump. The cathodic compartment was exposed to air under ambient “breathing” conditions and the performances of fuel cells were tested at 20 °C. Positive potentials were applied linearly using a linear sweep voltammetry to the cathode at a sweep rate of 2 mV s⁻¹ and the oxidation current was monitored with an anode as both counter and reference electrodes.

3. Results and discussion

3.1. Electrocatalytic oxygen reduction using the MWNT/PCo ink

To investigate the electrochemical performance of MWCNT/Nafion®/CoPc, the catalyst ink was deposited on a glassy carbon electrode by drop-casting. The catalytic activity of the immobilized CoPc complex for oxygen reduction was evaluated via a conventional three-electrode electrochemical setup. The experiments were conducted in 1.0 M KOH solution. Fig. 1 shows the CVs of the

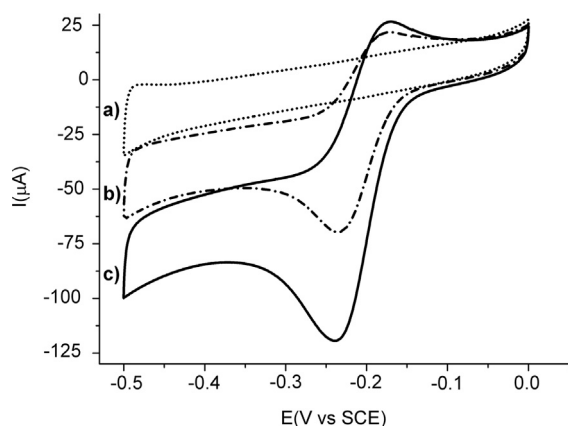


Fig. 1. Cyclic voltammograms of the catalytic MWCNT/Nafion/CoPc ink at 5 mV s⁻¹ scan rate in (a) argon, (b) air, and (c) O₂ saturated solution. The measurements were performed in 1 M KOH solution at 25 °C.

MWCNT/Nafion[®]/CoPc electrode at a scan rate of 5 mV s⁻¹ under oxygen, air, and argon, respectively. As expected, in the absence of oxygen (argon purged solution), no catalytic current was observed. The CV only reflects the featureless capacitive current of the MWCNT deposit, which was then used as a background signal to determine the catalytic current of the CoPc catalyst attached to the MWCNT sidewalls. In contrast, under air and oxygen, a catalytic current appears with an onset potential for oxygen reduction close to -0.14 V vs SCE (Figure S1). The latter slightly negatively shifted by only 60 mV compared with that observed with Pt/C catalyst under the same conditions.

To get more insight in the performance of our cathode, linear sweep voltammograms (LSVs) were carried out in alkaline media. Figure S1 shows the LSVs of CoPc modified GCE at 1 M KOH, (a) in ambient air (b) and in oxygen saturated 1 M KOH solution at a scan rate of 1 mV s⁻¹. Under oxygen saturated condition, the CoPc electrode exhibits a drastic increase in the intensity of the maximum cathodic current density compared with that of air condition, namely 1 mA cm⁻² instead of 0.55 mA cm⁻².

These studies demonstrate the appropriateness of CoPc as cathodic catalyst in alkaline solution. The excellent electrocatalytic properties MWCNT-supported CoPc catalyst towards O₂ reduction may result from the synergy of the high MWCNT surface area combined with the efficient electrocatalytic performance of CoPc. These performances highlight the importance of the MWCNTs, offering a high electronic conductivity to the resulting composite electrode material.

3.2. Morphological characterization of the MWCNT/CoPc cathode

The morphology of the catalytic composite layers at the cathode was examined by SEM. Fig. 2 shows SEM images of a pristine MWCNT deposit before and after modification by Nafion[®] and CoPc. Nafion[®] serves to reinforce mechanically the stability of MWCNT/CoPc composite as well as to entrap and firmly fix CoPc around the nanotubes. After deposition of the Nafion[®]/CoPc mixture, the MWCNTs appear thicker due to the homogeneous coating of the catalyst-polymer layer of 5–15 nm thickness. Taking into account that an excess of this polymer could drastically reduce the diffusion of air throughout the nanotube matrix and the electronic communication between nanotubes and catalyst, the composition of the MWCNT/Nafion[®]/CoPc mixture was optimized.

The SEM images confirm the highly porous structure of the nanotube deposit. The comparison of these images clearly indicates an overall homogeneous coating of the carbon nanotubes by Nafion and the catalyst which is a prerequisite condition for enhanced catalytic activity. Nevertheless, it should be noted that few agglomerates of a Nafion[®]/catalyst mixture are present (visible as bright droplets). There are also few parts where a polymeric layer incorporates small areas of the nanotube deposit. These morphological investigations reveal the efficiency of our deposition procedure but also give space for further optimization.

3.3. Fuel cell construction and performance

For the abiotic fuel cell device based on a Nafion[®] or Tokuyama membrane presented in this study, the anode is fixed in a chamber and operates in liquid phase supplied by a flow-through design. The continuous flow rate of 5 ml min⁻¹ diminishes substrate depletion and by-product accumulation, and allows mass transport investigations of the anode under fuel cell conditions. The cathode operates in gas phase (ambient air) that reduces the overcoming limitations associated with the low oxygen solubility in aqueous media. Ambient air was used since the membrane is sufficiently hydrated. The active area of the fuel cell based on Nafion[®] or Tokuyama membrane is of 5.76 cm². The outer area is of 53.72 mm² (Fig. 3A).

3.3.1. Effect of the ion exchange membrane on the glucose fuel cell performances: Nafion vs Tokuyama

Typical bell shaped curves showing the performances of the abiotic fuel cells based on an MWCNT/CoPc ink for the cathode and a classical C/Pt for the anode are presented in Fig. 3B. We used two different ion exchange membranes: a cation exchange membrane (Nafion[®]) which is often used in conventional polymer electrolyte

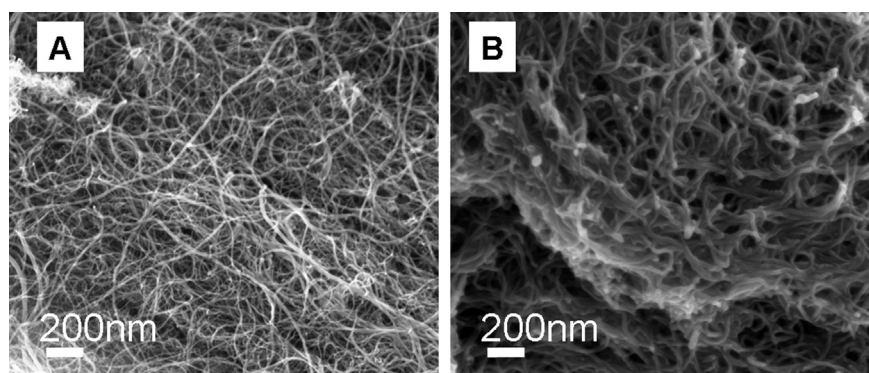


Fig. 2. Representative SEM images of (A) an unmodified MWCNT electrode and (B) an MWCNT/Nafion[®]/CoPc composite electrode.

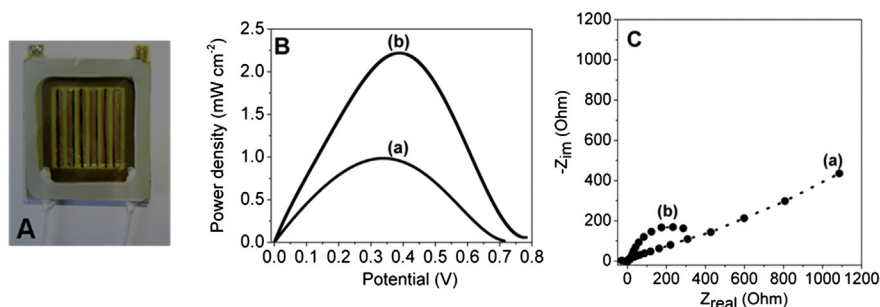


Fig. 3. (A) Photograph of the glucose fuel cell based on Nafion[®] and Tokuyama membranes. (B) Power density plots of a Glucose/air fuel cell using CNTs/PcCo catalyst as cathode and C/Pt as anode based on (a) a cation exchange membrane (Nafion[®]) and (b) a Tokuyama membrane. The flow rate of glucose is of 5 mL min⁻¹ and the cathode operates under air-breathing conditions. (C) Nyquist plots obtained from EIS measurements of the fuel cell based on (a) a Nafion[®] membrane and (b) a Tokuyama membrane. The frequency range is between 1000 kHz and 100 mHz.

fuel cells, and an anion exchange membrane (Tokuyama). The measured Open Circuit Voltage (OCV) is about 0.7 V for the Nafion[®] membrane and about 0.8 V for the Tokuyama membrane. The maximum power density is around 1 mW cm⁻² at 0.33 V for the Nafion[®] based fuel cell. The same experiments using the same amount of catalyst were performed with the Tokuyama anion exchange membrane. Compared with the Nafion[®] based fuel cell, the maximum power density increased more than two times to reach a value of 2.3 mW cm⁻² at 0.4 V.

In the present study, the anion exchange membrane (Tokuyama) and the cation exchange membrane (Nafion[®]) were used to avoid cross-reactions, because Pt nanoparticles present at the anode, are a poorly selective catalyst and can react with oxygen. However, the crossover of the aqueous glucose solution from the anode to the cathode through the electrolyte membrane will anyway happen in the case of polymeric membranes and should induce a decrease in the cell voltage and the fuel cell performance (water flooding).

It is well known that the glucose oxidation is more promoted in basic solutions due to the lack of specifically adsorbing ions in alkaline medium that may passivate metallic catalysts [6]. Moreover, glucose is oxidized to gluconic acid and the oxidation reaction is estimated to be a two electron process with the consumption of OH⁻ ions. The hydroxyl ions which are required for the glucose oxidation should migrate from the cathodic to the anodic side of the fuel cell. This is consistent with the involved hydroxide anions at this pH that is more efficiently conducted through the Tokuyama membrane compared to Nafion[®].

With the aim to deeply characterize the modified electrode, impedance measurements were used by plotting impedance data in terms of the real and imaginary components of impedance (Nyquist plots). A Nyquist plot can be used to investigate the

relative contributions of the membrane-only, electric-double-layer, and the diffusion-boundary layer resistances to the overall resistance occurring in the membrane–solution interface. From the Nyquist plots (Fig. 3C), it appears that the overall resistance and the solution resistance increased as the membrane resistance increased. The Nyquist plots show each two semi-circles indicating the double-layer resistance and the diffusion-boundary resistance, respectively from left to right. The second semi-circle was difficult to observe for Fig. 3C-(a) because the total resistance was very high for the cation exchange membrane Nafion[®]. These results corroborate to the low fuel cell performance obtained using Nafion[®] as ion exchange membrane. The total resistance is defined here as the sum of the real components of the impedance, namely the anode and cathode charge transfer resistances as well as the solution or electrolyte resistance. It clearly appears that Tokuyama membranes have a much lower charge transfer resistance than Nafion[®] membranes, which are commonly used as proton exchange membrane in alkaline conditions. The larger semi-circle indicates that the resistance of the diffusion-boundary layer was the dominant interface resistance as shown in Fig. 3C-(b).

One factor that contributes to low power density is the internal resistance of the fuel cell, which is associated with the ion transport between the electrodes and the electron transport through the electric circuit. The ion-transport resistance occurs in typical fuel cells configurations normally in solution and through the ion exchange membrane. The high-frequency resistances decreased also with decreasing membrane resistance. These points correspond to the minimum of the real part impedance, exhibited by the plots. Taking into account that the resistance decrease in solution seems dependent on the membrane type, this phenomenon may be related to ion transport.

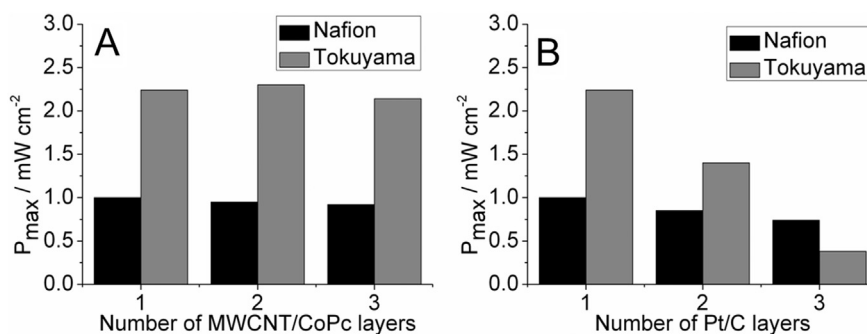


Fig. 4. Influence of the number of (A) MWCNT/CoPc layers and (B) C/Pt layers on the maximum power density of the glucose/air fuel cell based on (Nafion[®]) and Tokuyama ion exchange membranes.

3.3.2. Effect of the catalyst layer thickness

Different layers of C/Pt catalyst and MWCNT/CoPc were deposited on the Nafion® and Tokuyama membranes in order to improve the fuel cell performances. Spray coating of the catalyst affords a well control over the final quantity of the ink deposit. For the cathodic layer, the increase in the immobilized amount of catalyst has no effect on the performance of the fuel cells whatever the membranes used. This arises from the fact that oxygen reduction reaction limits the overall fuel cell performances.

On the other hand, increased C/Pt catalyst loading lowers the fuel cell efficiency (Fig. 4). Taking into account that the carbon black/Pt nanoparticles ink is not spread onto a porous MWCNT coating, the catalytic surface towards glucose oxidation remains limited to the C/Pt layer–solution interface. The increase of the deposited ink layer thickness may, in fact, increase steric hindrances for glucose permeation through the ink layer and hence increases the distance between the catalytic reaction and the underlying electron collector. Moreover, the thickness increase may also induce a decrease of the intrinsic conductivity of the catalytic ink layer.

To evaluate the efficiency of cobalt phthalocyanine as molecular cathodic catalyst, the maximum power densities, P_{\max} per mass unit of cathodic catalyst were calculated and compared with those recently reported for glucose fuel cell setups. Table S1 summarizes a comparison of these values and the OCP as well as the conditions required for these performances.

All of the studies, except the present work, used metallic catalysts for both, cathode and anode, while phthalocyanine cobalt was used in the present study. Some of the reported conditions employed elevated temperatures or/and high concentration of glucose or KOH. Despite such differences in the experimental conditions, it appears that the efficiency of the molecular cathodic catalyst is extremely high compared to those of other fuel cell setups using metal or metal alloys such as Ni-foams [13], active carbon [2], or stainless steel meshes [16]. The performances are comparable to those with Pt-based catalysts [15,17] and Ag/Ni-foams [12]; although it is lower than those with Pt–Ru [10] and HYPERMEC™ catalyst [14]. However, it should be noted that the molecular-catalysis fuel cell required only 0.006 mg cm^{-2} of cobalt metal. This metal amount is approximately 500 times below the amount of catalytic metal commonly used for glucose fuel cells. The power generated per mass unit of the cathodic catalyst was significantly higher (383 W g^{-1}) than those ($0.69\text{--}38 \text{ W g}^{-1}$) previously reported (Table S1). This performance highlights the advantage of the concept of glucose/ O_2 fuel cell using molecular catalyst as an alternative to metals or metal alloys. We also investigate the long-term stability of the fuel cell by measuring the power density during 50 days. The fuel cell still delivered 0.3 mW cm^{-2} after 50 days, which represents the highest stability reported until now for an alkaline glucose fuel cell.

4. Conclusion

We presented a new generation of non-enzymatic glucose fuel cell using an anionic exchange membrane. The fuel cell has a

maximum power density of 2.3 mW cm^{-2} at 0.4 V and a discharge current density of 8.6 mA cm^{-2} by using the Tokuyama anion exchange membrane. These performances were 2.3 times better than those recorded using a conventional Nafion membrane. The results suggest that the CoPc-catalyzed air-breathing cathode exhibits considerable electrocatalytic activity for oxygen reduction. In addition, we demonstrated that such design leads to the highest power densities per mass of catalyst. It is expected that these significant improvements in the functioning principle of glucose/oxygen fuel cells will be helpful for the development of a new generation of implantable fuel cells working in physiological media thus opening applications to the powering of implanted medical devices.

Acknowledgments

The authors would like to thank the platform “Functionalization of Surfaces and Transduction” of the scientific structure “Nanobio” for providing facilities. The authors also thank the ANR P2N-2010, project GLUCOPAC, and the ANR Investissements d’avenir – Nanobiotechnologies 10-IANN-0-02 programs for financial support. The present work was partially supported by the Labex ARCANÉ (ANR-11-LABX-0003-01).

Appendix A. Supplementary data

Supplementary data related to this article can be found in the online version at <http://dx.doi.org/10.1016/j.jpowsour.2013.12.109>.

References

- [1] S. Kerzenmacher, J. Ducrée, R. Zengerle, F. von Stetten, J. Power Sources 182 (2008) 1–17.
- [2] D. Basu, S. Basu, Electrochim. Acta 55 (2010) 5775–5779.
- [3] S. Kerzenmacher, U. Kräling, T. Metz, R. Zengerle, F. von Stetten, J. Power Sources 196 (2011) 1264–1272.
- [4] S.-i. Yamazaki, N. Fujiwara, S. Takeda, K. Yasuda, Chem. Commun. 46 (2010) 3607–3609.
- [5] A. Kozawa, V.E. Zilionis, R.J. Brodd, J. Electrochem. Soc. 117 (1970) 1474–1478.
- [6] K. Elouarzaki, A. Le Goff, M. Holzinger, J. Thery, S. Cosnier, J. Am. Chem. Soc. 134 (2012) 14078–14085.
- [7] K.A. Mauritz, R.B. Moore, Chem. Rev. 104 (2004) 4535–4586.
- [8] A.K. Sahu, S. Pitchumani, P. Sridhar, A.K. Shukla, Bull. Mater. Sci. 32 (2009) 285–294.
- [9] S.J. Peighambari, S. Rowshanzamir, M. Amjadi, Int. J. Hydrogen Energy 35 (2010) 9349–9384.
- [10] N. Fujiwara, S.-i. Yamazaki, Z. Siroma, T. Ioroi, H. Senoh, Electrochem. Commun. 11 (2009) 390–392.
- [11] S. Slade, S.A. Campbell, T.R. Ralph, F.C. Walsh, J. Electrochem. Soc. 149 (2002) 1556–1564.
- [12] J. Chen, C.X. Zhao, M.M. Zhi, K. Wang, L. Deng, G. Xu, Electrochim. Acta 66 (2012) 133–138.
- [13] C.X. Zhao, K. Wang, H. Yan, G. Xu, J. Electrochem. Soc. 158 (2011) B1055–B1059.
- [14] L. An, T.S. Zhao, S.Y. Shen, Q.X. Wu, R. Chen, J. Power Sources 196 (2011) 186–190.
- [15] K.-Y. Chan, X. Zhang, C.M. Lam, A.C.C. Tseung, P.K. Shen, J.K. You, Methods and apparatus for the oxidation of glucose molecules, 7419580, US, 2001.
- [16] N. Sano, T. Kodama, H. Tamon, Carbon 55 (2013) 365–368.
- [17] C.A. Appleby, D. Ingersoll, S. Sarangapani, M. Kelly, P. Atanassov, J. Electrochem. Soc. 157 (2010) 86–89.